# New Copper Phthalocyanine Oligomers for High Dielectric Constant Polymer Films

**Rituparna Saha, Braja K. Mandal**

*Department of Biological, Chemical, and Physical Sciences, Illinois Institute of Technology, Chicago, Illinois 60616*

**ABSTRACT:** We report here the synthesis of two new oligomeric copper phthalocyanine (CuPc) derivatives by esterification of the corresponding carboxylic acids with tri(ethylene glycol) monomethyl ether. The solubility of these derivatives in N,N′-dimethylformamide (DMF) enabled us to perform dielectric studies with poly(vinylidene fluoride-trifluoroethylene) P(VDF-TrFE), acting as the host polymer matrix. The highest room temperature dielectric constant achieved is 94 at 100 Hz, compared with 12 for the base polymer host matrix. Thermogravimetric analyzes of the polymer films showed that they are thermostable at 100°C for a long period of time. Scanning electron microscopy (SEM) images of the films have also been analyzed. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 122–128, 2010

**Key words:** composites; dielectric properties; host-guest systems

## INTRODUCTION

In recent years, there has been a growing demand for plastic electronics and plastic-based electromechanical and dielectric devices composed of polymers that are easy to process into mechanically robust components. Electroactive polymers with superior electromechanical responses have emerged as a promising class of materials with potential applications in the areas of flexible, lightweight, and low-cost electromechanical devices.[1–3] An important requirement for all these applications is high dielectric constant (high-$K$). However, polymers possess inherently low dielectric constants ($<15$).[4] This shortcoming of single-component polymer films has triggered extensive research to obtain polymer composite films by addition of a second component with a high dielectric constant. Composite films with good dielectric properties as well as good mechanical properties are now in great demand for fabrication of embedded capacitors for integrated electronic devices,[5–8] charge storage devices, and polymer actuators.[1,9]

Dielectric elastomers have generated a lot of interests as electroactive polymer actuators in wide range of applications, such as artificial muscles and sensors. These materials undergo large deformation while withstanding large forces. To increase the dielectric constant of such materials several approaches have been exercised. One approach is the incorporation of high dielectric constant inorganic ferroelectric ceramics (e.g., BaTiO$_3$) into a polymer matrix.[10–13] However, the use of inorganic fillers poses many disadvantages. For example, these ferroelectric ceramics are heavy, brittle, and require high temperature processing[14] leading to high costs, as well as showing poor adhesion with the polymer.[5] Since they possess a high elastic modulus, the final composite film, even with high-$K$, also has a significantly high elastic modulus and loses its flexibility, which is certainly not desirable in such applications. To overcome these issues, especially to increase the dielectric constant of such electroactive polymers without compromising their mechanical properties, recent research efforts have focused on organic compounds with high-$K$ as fillers. The most popular has been the CuPc oligomers. It has been reported that composite films filled with this class of organic materials exhibit mechanical properties similar to that of the unfilled polymer. For example, a P(VDF-TrFE) copolymer film with 40% (w/w) poly-CuPc showed a Young's modulus of ∼ 1000 mPA at room temeperature.[15]

CuPc oligomers are systems in which several CuPc units are fused to each other to form a planar disc-like structure. Such molecules exhibit very high room temperature dielectric constants, due to hyperelectronic nomadic polarization, as interpreted by Pohl et al.[16–18] This phenomenon can be defined as the movement of charges, in the presence of an external field, over one or more molecular lengths or several lattice sites due to the response of highly delocalized electrons. Dielectric properties of CuPc
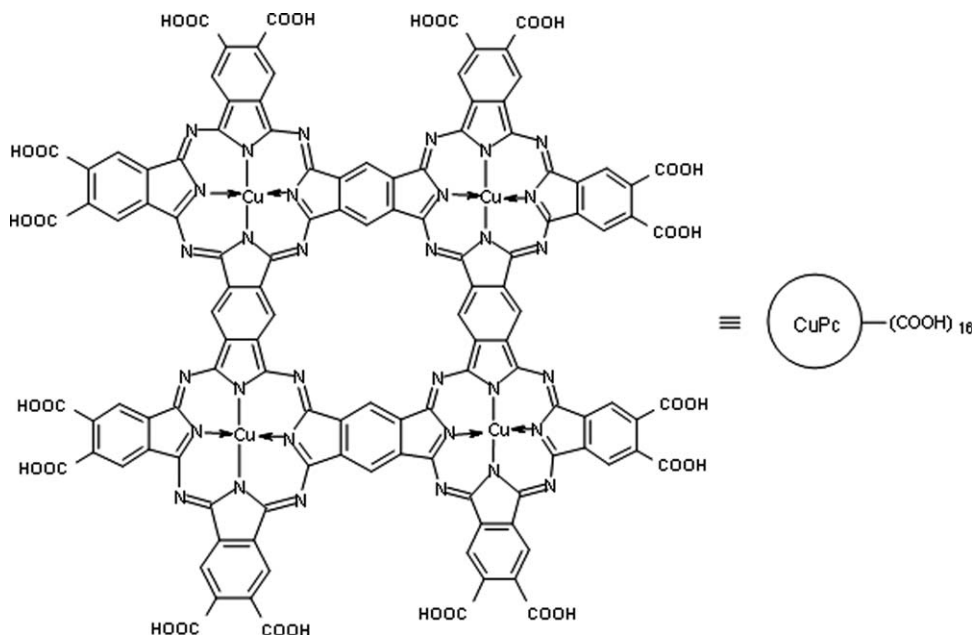
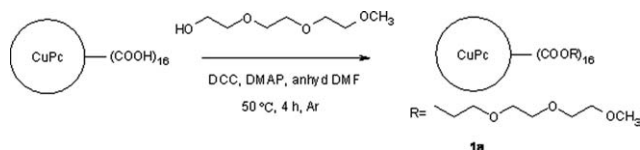**Figure 1** Structure of carboxylated CuPc oligomer (1).

oligomers, as a function of temperature and frequency, have been extensively studied.[19,20]

In this article, we report the synthesis and characterization of two new CuPc oligomers with improved solubility properties. Because of the presence of several oligo-ether groups at the peripheral site in these compounds, enhanced compatibility and/or higher loading with a polymer matrix is anticipated. Indeed, when they were dispersed in a P(VDF-TrFE) copolymer matrix, the dielectric constant values of the composite polymer films were significantly increased.

## EXPERIMENTAL

### Synthesis of tri(ethyleneglycol)monomethyl ether capped CuPc oligomer

In a typical reaction procedure, tri(ethyleneglycol) monomethyl ether (5 g, 0.03 mol) and carboxylated CuPc oligomer 1 (Fig. 1) (2.25 g, 0.871 mmol) were placed in a 50 mL three-neck round-bottom flask fitted with a condenser and dissolved in 25 mL anhydrous DMF in an argon atmosphere at 50°C. The temperature was then brought down to room temperature. 4-dimethylaminopyridine (DMAP) (0.25 g, 0.002 mol), was added followed by dicyclohexylcar-

bodiimide (DCC) (4 g, 0.02 mol) at 10°C. The solution was stirred at 60°C for 4 h. After the reaction, the mixture was cooled to room temperature and poured into 500 mL of diethyl ether. The dark green solid was collected by centrifugation, washed with ether to remove traces of tri(ethyleneglycol) monomethyl ether and DMAP. It was then dissolved in chloroform and filtered to remove N,N'-dicyclohexyl urea, the byproduct of the reaction. Chloroform was evaporated to give the dark bluish green solid product 1a (Scheme 1).

### Synthesis of poly-tri(ethyleneglycol)monomethyl ether capped CuPc

Poly-CuPc (2) (Fig. 2) (0.8 g) was dissolved in 30 mL of concentrated sulfuric acid at 60°C for 2 h, and then poured into excess water, washed thoroughly, with water and dried at 60°C under vacuum to give a dark blue solid product 2a (Scheme 2). This was then capped with triethyleneglycol monomethyl



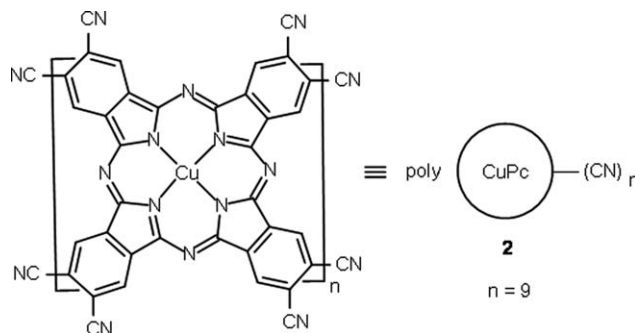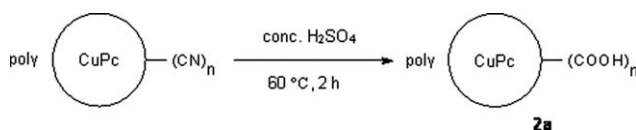**Scheme 1** Synthesis of tri(ethyleneglycol)monomethyl ether capped CuPc oligomer (1a).



**Figure 2** Structure of cyanated CuPc polymer (2).

**Scheme 2** Hydrolysis of poly (CuPc) **(2)**.

ether, following the procedure described above. Hydrolyzed product (0.75 g) was taken in a 50 mL round bottom flask along with excess triethyleneglycol monomethyl ether (9 g, 54.8 mmol). DMAP (0.225 g) and DCC (2.25 g, 0.85 mol) were added and the esterification reaction carried out in melt condition at 100°C overnight in the presence of Ar. After the reaction, the mixture was poured into excess ether and centrifuged, then washed several times with ether to remove unreacted triethyleneglycol monomethyl ether and DMAP. The solid was then dissolved in DMF and filtered to remove N,N′-dicyclohexylurea. DMF was evaporated at 50°C under reduced pressure to give 0.85 g of the final product **2b**, a dark bluish green solid (Scheme 3).

## Preparation of P(VDF-TrFE)-CuPc composite films

P(VDF-TrFE) [51/49% P(VF2-VF3)] (purchased from KTech corp) was used as the base polymer. Films were made with 30, 50, and 70% loading (weight percent) of the CuPc esters **1a** and **2b**. P(VDF-TrFE) was first dissolved in a minimum amount of DMF and a calculated amount of CuPcs was added, and the mixture was allowed to dissolve over 24 h with stirring. The solution was then poured onto a Teflon Petridish and dried in air for 4 h, followed by vacuum drying at 70°C overnight, to obtain thin films which were then hot-pressed (Carver Laboratory Press) at 150°C using a spacer of 0.01 mm thickness. The films were cut into circles of 20 mm diameter for dielectric constant measurements. These films were also used for thermogravimetric analyses (TGA) and scanning electron microscopy (SEM).

## RESULTS AND DISCUSSION

### Synthesis

Tri(ethyleneglycol)monomethyl ether capped CuPc oligomer (**1a**) was prepared by esterification of carboxylated CuPc sheet oligomer with excess of tri(ethyleneglycol)monomethyl ether. **1** was synthesized from pyromellitic dianhydride, copper sulfate pentahydrate, urea, ammonium chloride, and ammonium molybdate, following the procedure reported by Achar et al.[21] The esterification was carried out in the presence of DCC and a catalyst, DMAP. The solvent for the reaction was N,N′-dimethylformamide (DMF).

The second ester derivative, tri(ethyleneglycol)monomethyl ether capped CuPc polymer (**2b**) was prepared in two steps. Commercially available CuPc polymer, having cyano (C≡N) functional groups (verified by FTIR), was purchased from Aldrich. It was carefully hydrolyzed to its carboxylated analog (**2a**). A mild condition for hydrolysis using concentrated sulfuric acid ($H_2SO_4$) was developed that gave fully hydrolyzed product without cleaving the macrocyclic ring. This polymeric CuPc was selected because of the presence of more Pc fused rings compared to **1**, which will result in more delocalization of electrons. However, even after hydrolysis, the hydrolyzed product **2a** was not soluble in DMF, our preferred solvent for the following esterification reaction. Consequently, the esterification reaction was carried out with a large excess of tri(ethyleneglycol)monomethyl ether using DCC and DMAP, without using any solvent.

The carboxylated CuPc oligomer **1** is soluble in DMF, DMSO, and $H_2SO_4$, and the commercially available poly-CuPc **2** is soluble only in $H_2SO_4$ and partially in DMSO, but both of them are insoluble in common organic solvents such as chloroform, methylene chloride, and methanol. By contrast, after the esterification, the solubility of both **1a** and **2b** is improved compared with their Pc precursors. **1a** is fully soluble in chloroform and methanol while **2b** is partially soluble in these solvents and readily soluble in DMF. Improved solubility is attributed to the presence of several aliphatic side chains.

The CuPcs were characterized by FTIR spectroscopy using a Thermo Nicolet Nexus 470 FTIR spectrometer. The infrared spectrum of **1a** shows strong peaks at 2928 cm$^{-1}$ and 2850 cm$^{-1}$, which are indicative of the $CH_2$ asymmetric and $CH_2$ symmetric stretching vibration frequencies, respectively. These two peaks are absent in the spectrum of **1**. A sharp peak at 1722 cm$^{-1}$ in **1a** is due to the ester carbonyl group. The FTIR spectrum of the commercially available poly CuPc **2** exhibits a strong sharp peak at 2228 cm$^{-1}$, indicative of cyano groups. After hydrolysis, this peak disappears and a new peak appears at 1705 cm$^{-1}$, assignable to the C=O of the carboxylic acid functional group. The presence of a broad absorption band due to O—H stretching in the region 2400–3200 cm$^{-1}$ also supports the hydrolysis of cyano groups to carboxylic acids. The infrared spectrum of **2b** is proof of a successful esterification
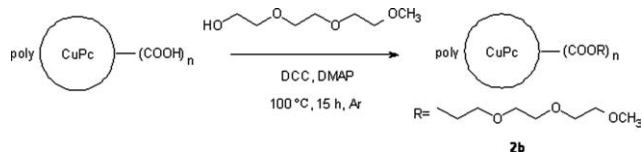


**Scheme 3** Synthesis of poly-tri(ethyleneglycol)monomethyl ether capped CuPc **(2b).**

reaction with the disappearance of the broad O—H stretching absorption band and presence of strong peaks at 2924 cm$^{-1}$ and 2850 cm$^{-1}$ for CH$_2$ asymmetric and CH$_2$ symmetric stretching vibration frequencies, respectively. The peak at 1718 cm$^{-1}$ is for the ester carbonyl group, thus providing evidence that the esterification reactions have succeeded.

The structures of **1a** and **2b** were also verified from their $^1$H-NMR spectra in (methyl sulfoxide)-d$_6$ with Bruker 300. Besides aromatic protons at δ = 7.95, the methyl (—CH$_3$) protons showed a peak at δ = 3.22 (s) in **1a** and at δ = 3.23 (s) in **2b**. The chemical shifts for the —CH$_2$- protons were recorded at δ = 3.33 (m) for **1a** and δ = 3.37 (m) for **2b**.

Typically for CuPcs, in UV-vis spectra, there is a strong absorption between 670 and 690 nm, known as the Q band and another strong absorption band between 320 and 370 nm, denoted as the B band. The UV absorption spectrum of **1a** exhibits a sharp Q band at 692 nm and the B band at 352 nm. Chloroform was used as a solvent. The commercially available poly CuPc **2** has the Q band at 685 nm and the B band at 346 nm. The aborption remains the same in the hydrolyzed product **2a** and in the TEG-capped product **2b**, the Q band appearing at 678 nm in both of them and the B band at 349 nm in **2a** and 347 nm in **2b**. DMSO was used as a solvent in this case. These observations demonstrate that there is no change in the chromophore due to subsequent hydrolysis and esterification reactions. The UV spectra were taken by Perkin Elmer (UV/VIS/NIR) spectrometer Lambda 19.

### Thin-film preparation

Poly(vinylidene fluoride) based copolymers, such as P(VDF-TrFE), have been used as the polymer matrix because their room temperature dielectric constants are among the best.[22–27] It also possesses good piezoelectric properties that make it ideal for a broad range of electrical applications. Consequently, in this study, we have used P(VDF-TrFE) as the polymer host. The solution cast method was used to prepare the polymer composite films. The hot-press technique was used to obtain composite films with thickness around 0.01 mm.

### Dielectric properties

Dielectric constants of the composite films were measured at room temperature using a Solartron 1296 Dielectric Interface. The room temperature frequency dependence of dielectric constant of the films was measured at AC level of 100 mV in the frequency range of 1 Hz–1 MHz. The changes in relative permittivity (dielectric constant) with frequency are shown in Figure 3. The dielectric con-

stant of P(VDF-TrFE) copolymer at room temperature is found to be 12 at 100 Hz. At that frequency, the room temperature dielectric constant values of the polymer films with 30, 50, and 70% loading (by weight) of **1a** are 28, 50, and 53, respectively. The dielectric constant values at 100 Hz of the P(VDF-TrFE) films with 30, 50, and 70% loading (by weight) of **2b** are 57, 66, and 94 respectively, a significant increase over the base copolymer value. For all films, the dielectric constant continuously increases with the decrease in frequency values.

In spite of having a high dielectric constant, CuPc oligomers have high dielectric loss which is undesirable in all practical applications. The high dielectric loss can be attributed to the long-range intermolecular hopping of electrons.[28] However, when it is dispersed into the P(VDF-TrFE) matrix, the polymer matrix acts as an insulation layer to the CuPc particulates, resulting in a substantial decrease of dielectric loss in the composite films. The dielectric losses are below 1 between 10 Hz and 1 MHz for films with 30 and 50 wt % of **1a**. The film with 70 wt % of **1a** shows a very high dielectric loss (2–4) at lower
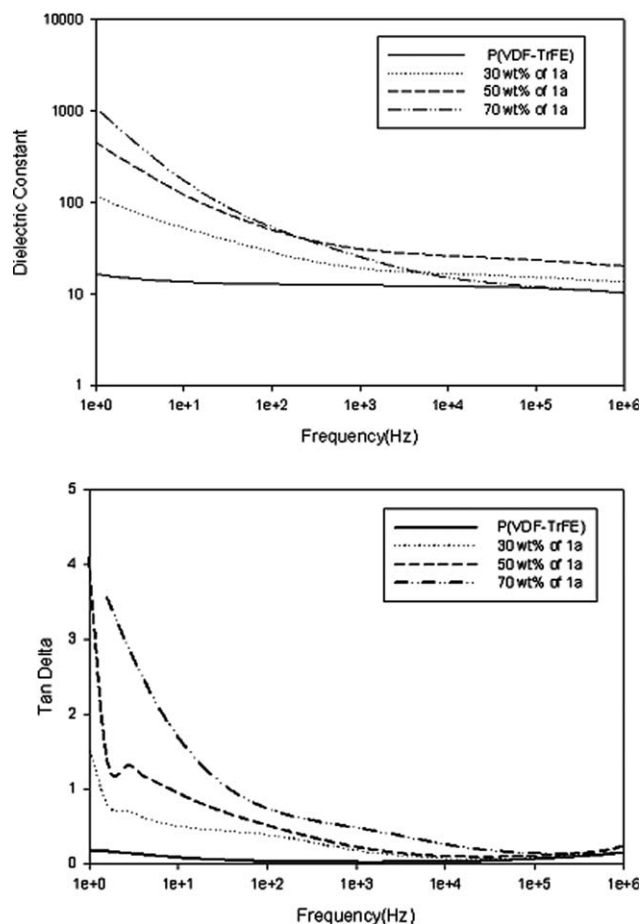


**Figure 3** Room temperature dielectric constant and dielectric loss of the base polymer and the composite films containing **1a**.
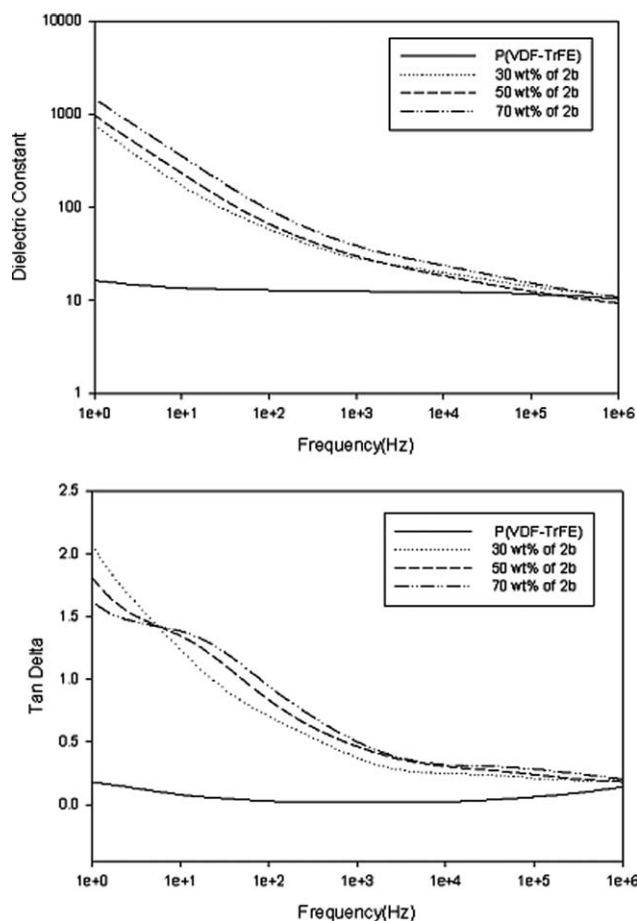
**Figure 4** Room temperature dielectric constant and dielectric loss of the base polymer and the composite films containing **2b**.

frequencies but it decreases with increase in frequency and drops below 1 at 40 Hz (Fig. 3). For the set of films with **2b**, the dielectric losses are between 1.0 and 1.6 at the lower frequencies (<100 Hz) and are less than 1.0 in the range of 100 Hz–1 MHz (Fig. 4).

## Surface morphology

The surface morphology of the films was studied using (SEM) by a JEOL JSM5900-LV instrument. Since the films contain CuPc, which is semi-conducting, it was not necessary to deposit conducting coating on the films. They were directly placed on the sample holder, and images were taken at different magnifications. Figure 5 shows the SEM images of the composite films containing different weight percents of **1a**. The SEM image of the film containing 30 wt % of **1a** shows almost evenly distributed granular morphology with very little fiber-like structures [Fig. 5(a)]. On the other hand, the film with 70 wt % of **1a** [Fig. 5(c)], shows a total change in morphology. This film is dominated by lots of fibrous structures and with almost no grains. The morphology is

more homogeneous than the films with 30% and 50% loading. The film with 50 wt % of **1a** [Fig. 5(b)] consists of granular structures and fibrous structures and is probably in the process of undergoing the transformation from granular to fibrous morphology.
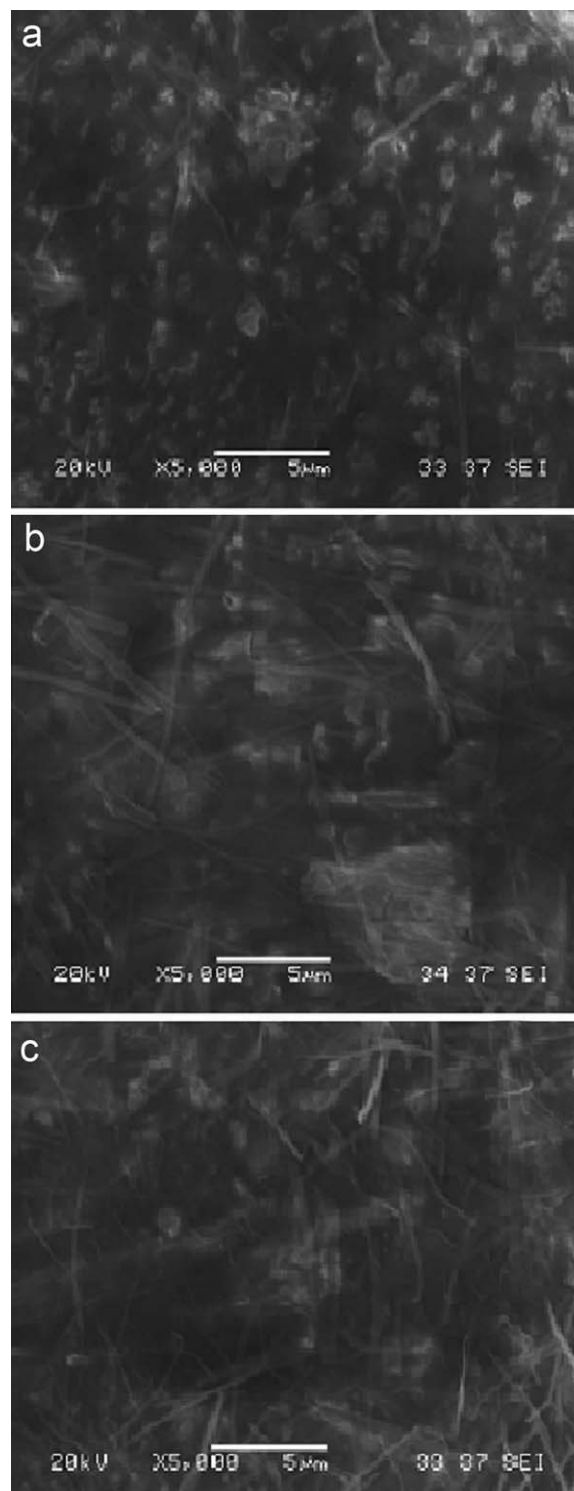


**Figure 5** (a) SEM image of film containing 30 wt % of **1a**. (b) SEM image of film containing 50 wt % of **1a**. (c) SEM image of film containing 70 wt % of **1a**.
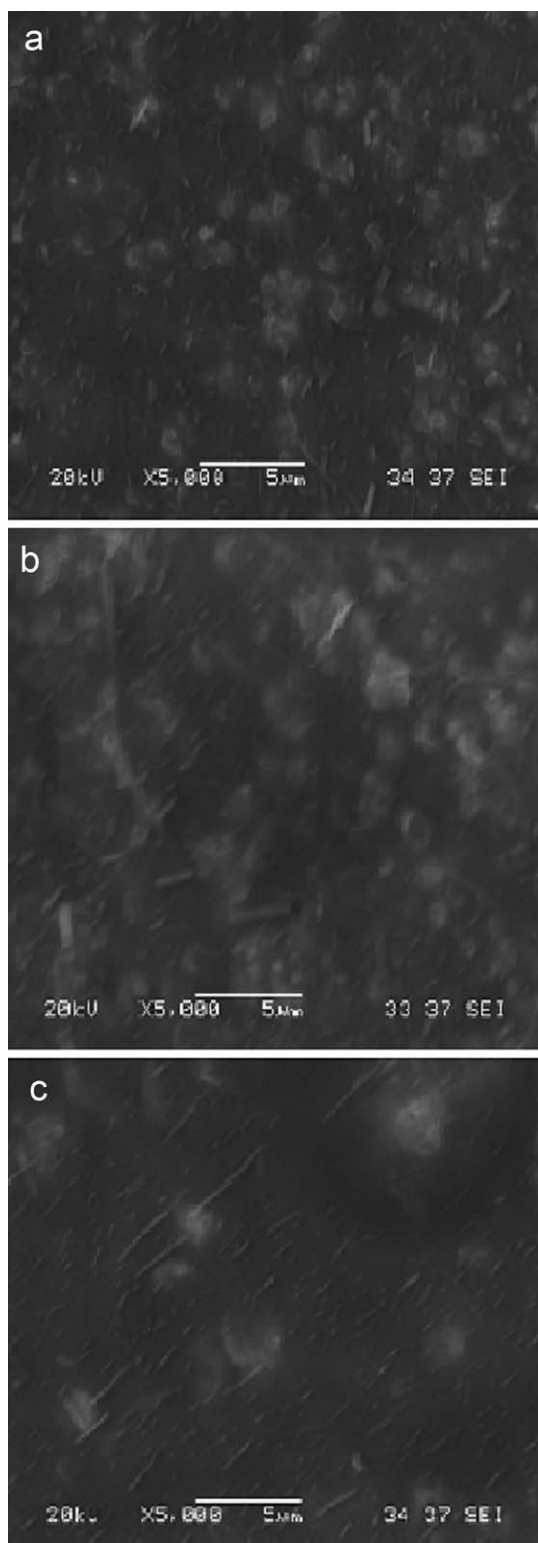
**Figure 6** (a) SEM image of film containing 30 wt % of **2b**. (b) SEM image of film containing 50 wt % of **2b**. (c) SEM image of film containing 70 wt % of **2b**.

The composite films containing **2b** show a similar trend in the morphology transformation with change in weight percent of **2b**, as shown by films with **1a**. In the film containing 30 wt % of **2b** [Fig. 6(a)], there are
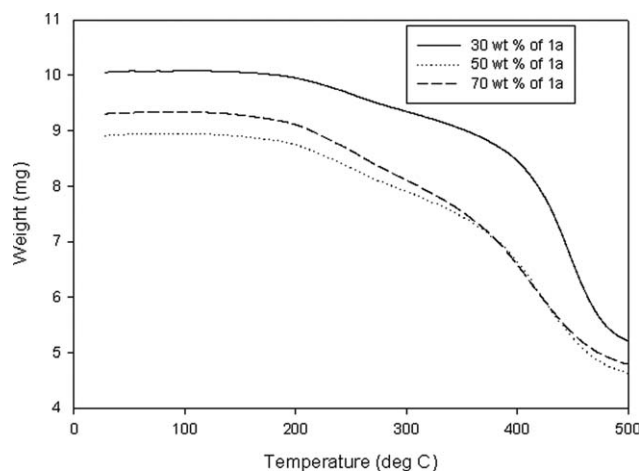


**Figure 7** Thermograms of the composite films containing **1a**.

small grains as well as small fiber or needle like structures. At 50 wt % loading, the grains are bigger in size, and it seems that the fiber like structures have started to get organized in a particular orientation [Fig. 6(b)]. When the loading is 70 wt %, the grains are sparse, and the needle-like fibers exhibit a regular alignment (parallel to each other) [Fig. 6(c)]. It should be noted that this granular to fibrous morphology transition was not induced by shear. This was observed to be the property of the composite films, because the pictures presented here were not obtained from torn films. They represent the top view of their surfaces.

## Thermal properties

The thermal stability of the composite films containing **1a** and **2b** were investigated by a thermogravimetric analyzer (TGA), a Mettler Toledo system TGA/SDTA 851e. Around 8–10 mg of sample was heated from 25°C to 500°C at a heating rate of 10°C/min. The loss in weight (in mg) of sample with
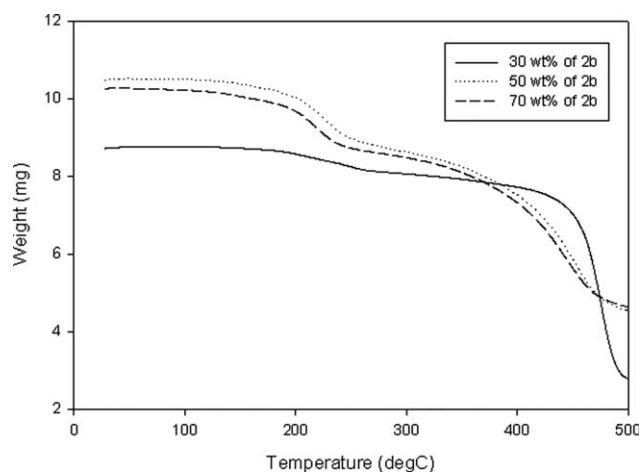


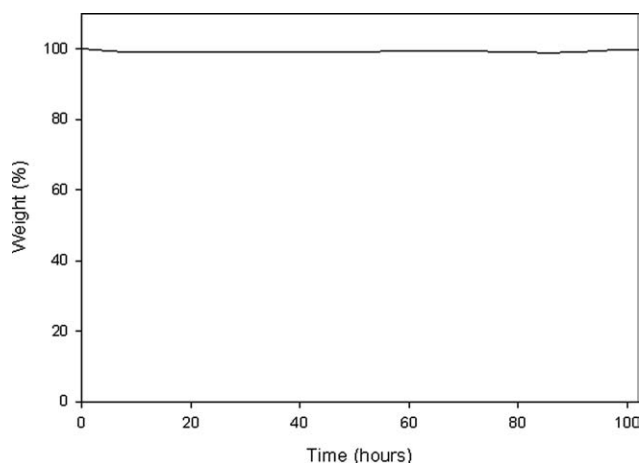**Figure 8** Thermograms of the composite films containing **2b**.

**Figure 9** Isothermal study at 100°C of the composite film containing 50 wt % of **1a**.

increase in temperature is shown in Figures 7 and 8. All the films were found to be thermally stable up to 150°C (<0.1% weight loss). An isothermal analysis, with a representative film [P(VDF-TrFE) with 50 wt % of **1a**], was also performed to determine the long-time thermal stability of these composites. We noticed no degradation of the sample at 100°C for 100 h (Fig. 9).

## CONCLUSIONS

Two new CuPc oligomers with good solubility properties were synthesized. They were blended with P(VDF-TrFE) copolymer to make composite films with improved dielectric properties. The films were homogenous and long term thermally stable at 100°C. The new CuPcs were characterized by various spectroscopic methods.

## References

1. Bar-Cohen, Y., Ed. Electroactive Polymers (EAP) Actuators as Artificial Muscles—Reality, Potential, and Challenges, 2nd ed.; SPIE: Bellingham, WA, 2004.
2. Xu, T. B.; Cheng, Z. Y.; Zhang, Q. M. Appl Phys Lett 2002, 80, 1082.
3. Zhang, Q. M.; Bharti, B.; Zhao, X. Science 1998, 280, 2101.
4. Bandrup, J. Polymer Handbook, 2nd ed.; Wiley-Interscience: New York, 1974; p VIII-7.
5. Rao, Y.; Wong, C. P. In Proceedings of IEEE Polytronic 2002; p 196–200.
6. Rao, Y.; Wong, C. P. J Appl Polym Sci 2004, 92, 2228.
7. Bhattacharya, S. K.; Tummala, R. R. J Mater Sci Mater Electron 2000, 11, 253.
8. Chahal, P.; Tummala, R. R.; Allen, M. G.; Swaminathan, M. IEEE Trans Comput Pack Manuf Technol Part B: Adv Packaging 1998, 21, 184.
9. Nalwa, H. S., Ed. Handbook of Low and High Dielectric Constant Materials and Their Applications; Academic: San Diego, CA, 1999.
10. Chiang, C. K.; Popielarz, R. Ferroelectrics 2002, 275, 1.
11. Chahal, P.; Tummala, R.; Allen, M. G. In International Symposium on Microelectronics; SPIE: Orlando, FL, 1996; p 126–131.
12. Tummala, R. R.; Chahal, P.; Bhattacharya, S. In IMAPS 35th Nordic Conference; Sweden, 1998.
13. Rao, Y.; Ogitani, S.; Kohl, P.; Wong, C. P. J Appl Polym Sci 2002, 83, 1084.
14. Dimos, D.; Lockwood, S. J.; Schwarz, R. W.; Rodgers, M. S. IEEE Trans Comput Hybrids Manuf Technol 1994, 18, 174.
15. Szabo, J. P.; Hiltz, J. A.; Cameron, C. G.; Underhill, R. S.; White, B.; Leidner, J. Proc SPIE 2003, 5051, 180.
16. Pohl, H. A. IEEE Trans Electr Insul 1986, 21, 683.
17. Rosen, R.; Pohl, H. A. J Polym Sci Part A-1: Polym Chem 1966, 4, 1135.
18. Pohl, H. A.; Pollak, M. J Chem Phys 1977, 66, 4031.
19. Nalwa, H. S.; Dalton, L. R.; Vasudevan, P. Eur Polym J 1985, 21, 943.
20. Tewari, U. S.; Sharma, S. K.; Nalwa, H. S.; Vasudevan, P. IEEE Trans Electron Instrum 1985, EI-20, 975.
21. Achar, B. N.; Fohlen, G. G.; Parker, J. A. J Polym Sci Polym Chem 1982, 20, 1785.
22. Huang, C.; Zhang, Q. M.; Su, J. Appl Phys Lett 2003, 82, 3502.
23. Xu, H.; Bai, Y.; Bharti, V.; Cheng, Z.-Y. J Appl Polym Sci 2001, 82, 70.
24. Wang, J.-W.; Shen, Q.-D.; Bao, H.-M.; Yang, C.-Z. Macromolecules 2005, 38, 2247.
25. Wang, J.-W.; Shen, Q.-D.; Yang, C.-Z. Macromolecules 2004, 37, 2294.
26. Bobnar, V.; Levstik, A.; Huang, C.; Zhang, Q. M. Phys Rev Lett 2004, 92, 47604.
27. Huang, C.; Zhang, Q. Adv Mater 2005, 17, 1153.
28. Gould, P. D. Coord Chem Rev 1996, 156, 237.